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Speeds of sound and isentropic compressibilities of binary mixtures containing dipropylene glycol monobutyl ether with n-alkanols at 298.15 K

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Abstract : Speeds of sound have been measured in dipropylene glycol monobutyl ether + methanol, 1-propanol, 1-pentanol, 1-heptanol, across the entire composition range, at the temperature 298.15 K and atmospheric pressure. The speed of sound values were combined with excess molar volume to obtain values for the product $K_{S,m}$ of the molar volume and the isentropic compressibility κ_S, and the corresponding quantities $K_S{}^E{}_m$ were also calculated. The $K^E_{S,m}$ values are negative for all mixtures. The deviation of the speeds of sound u^D from their values u^{id} in ideal mixtures were obtained for all measured mole fractions. These values are compared with mixing function δu. The behaviour of u, δu, u^D, and $K^E_{S,m}$ as a function of composition and number of carbon atoms in the alcohol molecule is discussed.

Keywords : Binary mixtures, acoustical parameters, molecular interactions.

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1. Introduction

In continuation of our programme of research on the physico-chemical properties of binary mixtures containing the oxygen (-O-) and hydroxyl (-OH) functional group [1-5], we report here experimental values of the speed of sound for mixtures of dipropylene glycol monobutyl ether with methanol, 1-propanol, 1-pentanol, or 1-heptanol at 298.15 K and atmospheric pressure. The isentropic compressibilities κ_S for all mixtures were estimated by combining the densities derived from the excess molar volumes [4,5] and the speeds of sound. The molar volume were multiplied by the isentropic compressibilities to obtain estimates of $K_{S,m}$. We have also calculated the deviations u^D of the speeds of sound from those u^{id} in the ideal mixtures, together with the excess molar quantities $K_S{}^E{}_m$ and the mixing function δu.

2. Experimental

Dipropylene glycol monobutyl ether (Aldrich, mass fraction > 0.99) was used as received. Spectroscopic grade alcohols were dried and fractionally distilled as described elsewhere [6]. Prior to measurements, all liquids were stored in dark bottle over 0.4 nm molecular sieve to reduce water content, and were partially degassed at low pressure. The purities of the liquids were checked by comparing the densities at 298.15 K with their corresponding literature values (Table 1). Also given in Table 1 are measured or literature values [6–20] of these quantities which were required in the estimation of $K_{S,m}$, $K^E_{S,m}$, and u^D. The densities were measured with a single stem pycnometer that gave an estimated reproducibility of 3×10^{-2} kg m^{-3} at 298.15 K. The mole fraction of each mixture was obtained to an accuracy of 1×10^{-4} from the measured apparent masses of the components. All masses were corrected for buoyancy. All molar quantities were based upon the IUPAC table of atomic weights [21].

Ultrasonic speeds of pure liquids and their mixtures at 298.15 K were measured using a NUSONIC (Mapco, Model 6080) velocimeter based on the sing round technique [22] with 4 MHz acoustic waves. The maximal

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Table 1. Observed and literature values of densities (ρ^*), isobaric thermal expansivities (α_p^*), molar isobaric heat capacities ($C_{p,m}^*$) ultrasonic speeds (u^*), and the product $K_{S,m}^*$ of molar volume and isentropic compressibility of pure liquid components at 298.15 K.

Components	ρ^* (kg m^{-3})		α_p^*	$C_{p,m}^*$	u^* (ms^{-1})		$K_{S,m}^*$
	obs.	lit.	(kK^{-1})	(J K^{-1} mol^{-1})	obs	lit.	(mm^3 mol^{-1} MPa^{-1})
Dipropylene glycol monobutyl ether	908.65	908.9 [7]	0.886[a]	381.9[b]	1279.3		140.82
Methanol	786.45	786.5 [8]	1.201 [10]	81.21 [9]	1105.6	1102.8 [11]	42.38
		786.38 [9]				1103 [12]	
		786.54 [6]					
1-Propanol	799.61	799.62 [13]	1.003 [10]	144.10 [9]	1209.7	1206.4 [15]	64.23
		799.59 [14]					
		799.57 [18]					
1-Pentanol	811.12	811.10 [18]	0.893 [16]	208.4 [17]	1275.0	1275.18 [18]	82.42
		811.15 [6]				1275.5 [19]	
1-Heptanol	819.21	818.9 [20]					
		819.50 [6]	0.845[a]	271.7[b]	1327.7		98.23

[a]calculated from our measured densities; [b]estimated using group additivity.

error in the measurements of the sound speed relative to water (1496.687 ms^{-1}) at 298.15 K [23] is estimated to be less 0.2 ms^{-1}. Further details concerning this apparatus, its calibrations, and operating procedure have been described previously [24,25]. All the measurements were carried out in well-stirred water-bath with temperature controlled to ±0.01 K.

3. Results and discussion

Table 2 gives the experimental results of speed of sound at 298.15 K of all the binary mixtures at various mole fractions of x_1. This property has not been reported previously.

The measured speeds of sound u were fitted to a polynomial of type :

$$u = \sum_{i=0}^{k} a_i x_1^i , \qquad (1)$$

by the method of least-squares with each point weighted equally. The values of coefficients a_i and standard deviations σ are summarized in Table 3(a).

The κ_S and $K_{S,m}$ have been calculated from the relations :

$$\kappa_s = (\rho u^2)^{-1} = V(M u^2)^{-1}, \qquad (2)$$

$$K_{S,m} = -(\partial V/\partial p)_s = V \cdot \kappa_S = \Sigma x_i M_i/(\rho u)^2, \qquad (3)$$

where x_i and M_i are respectively the mole fraction and molar mass of component in a mixture with density ρ, and V is the molar volume.

The excess quantities $K_{S,m}^E$ were calculated from [26,27] :

$$K_{S,m}^E = K_{S,m} - K_{S,m}^{id} \qquad (4)$$

Table 2. Ultrasonic speed u, and the product $K_{S,m}$ of the molar volume and isentropic compressibility for liquid mixtures at 298.15 K.

x_1	u (ms^{-1})	$K_{S,m}$ (mm^3 mol^{-1} MPa^{-1})	x_1	u (ms^{-1})	$K_{S,m}$ (mm^3 mol^{-1} MPa^{-1})
x_1 $C_4H_9[O(CH_2)_3]_2OH$ + x_2 CH_3OH					
0.0022	1107.5	42.53	0.4213	1254.4	79.52
0.0072	1111.7	42.88	0.4739	1259.8	84.77
0.0139	1117.5	43.33	0.5095	1262.9	88.36
0.0233	1125.0	43.99	0.5514	1265.9	92.65
0.0317	1131.4	44.59	0.5932	1268.3	96.99
0.0396	1137.1	45.17	0.6290	1270.0	100.74
0.0492	1143.9	45.88	0.6736	1271.8	105.46
0.0604	1151.6	46.70	0.7249	1273.4	110.96
0.0810	1164.0	48.30	0.7817	1275.3	117.01
0.0910	1169.1	49.13	0.8302	1276.6	122.23
0.1274	1186.3	52.16	0.8963	1277.9	129.42
0.1690	1206.6	55.37	0.9288	1278.5	132.96
0.2375	1222.5	61.95	0.9590	1278.8	136.31
0.2887	1234.4	66.67	0.9786	1279.2	138.43
0.3289	1241.7	70.50	0.9924	1279.1	140.01
0.3799	1249.3	75.45			
x_1 $C_4H_9[O(CH_2)_3]_2OH$ + x_2 C_3H_7OH					
0.0060	1210.1	64.71	0.5284	1268.9	102.41
0.0118	1211.1	65.11	0.5778	1270.8	106.32
0.0215	1212.5	65.80	0.6370	1272.8	111.04
0.0347	1215.8	66.60	0.6904	1274.4	115.32
0.0568	1222.3	67.80	0.7351	1275.3	118.97
0.0783	1226.6	69.18	0.7784	1276.4	122.46
0.1043	1231.3	70.90	0.8214	1277.2	125.98
0.1464	1237.9	73.76	0.8617	1277.8	129.30
0.2038	1245.6	77.77	0.9007	1278.4	132.51
0.2710	1252.4	82.68	0.9174	1278.5	133.92

Table 2. *Cont'd.*

0.3082	1255.7	85.44	0.9446	1278.9	136.16
0.3582	1259.6	89.20	0.9719	1278.9	138.50
0.4276	1263.9	94.54	0.9968	1279.2	140.57
0.4821	1266.8	98.77			
		x_1 $C_4H_9[O(CH_2)_3]_2OH + x_2$ $C_5H_{11}OH$			
0.0039	1275.1	82.62	0.4208	1281.6	105.52
0.0110	1275.2	82.99	0.4680	1281.9	108.25
0.0219	1275.3	83.57	0.5205	1281.9	111.35
0.0311	1275.7	84.02	0.5672	1281.9	114.13
0.0430	1276.1	84.63	0.6216	1281.9	117.37
0.0552	1276.5	85.25	0.6874	1281.7	121.34
0.0661	1276.8	85.81	0.7248	1281.5	123.62
0.0773	1277.3	86.37	0.7751	1281.1	126.73
0.0977	1277.9	87.43	0.8312	1280.6	130.23
0.1470	1278.6	90.11	0.8765	1280.3	133.04
0.1852	1279.2	92.21	0.9048	1280.1	134.81
0.2145	1279.7	93.81	0.9363	1279.8	136.80
0.2668	1280.5	96.71	0.9497	1279.5	137.68
0.3067	1280.9	98.96	0.9768	1279.4	139.37
0.3709	1281.4	102.63	0.9967	1279.3	140.68
		x_1 $C_4H_9[O(CH_2)_3]_2OH + x_2$ $C_7H_{15}OH$			
0.0060	1327.5	98.43	0.4784	1301.0	117.93
0.0142	1327.1	98.73	0.5432	1298.0	120.70
0.0234	1326.4	99.10	0.5831	1296.1	122.44
0.0363	1325.5	99.61	0.6404	1293.7	124.89
0.0494	1324.6	100.13	0.6817	1291.5	126.77
0.0638	1323.6	100.72	0.7304	1289.6	128.87
0.0807	1322.4	101.41	0.7746	1287.8	130.81
0.1003	1321.1	102.21	0.8145	1286.0	132.61
0.1471	1318.1	104.31	0.8813	1283.6	135.53
0.1991	1315.1	106.27	0.9125	1282.2	136.97
0.2308	1313.1	107.60	0.9425	1281.2	138.28
0.2788	1310.7	109.55	0.9634	1280.5	139.20
0.3287	1308.0	111.66	0.9827	1279.9	140.05
0.3973	1304.8	114.50	0.9970	1279.4	140.69
0.4394	1302.9	116.26			

where

$$K^{id}_{S,m} = \Sigma x_i \left[K^*_{S,i} - T A^*_{p,i} \left\{(\Sigma x_i A^*_{p,i} / \Sigma x_i C^*_{p,i}) - (A^*_{p,i} / C^*_{p,i})\right\}\right]. \quad (5)$$

where, $A^*_{p,i}$ (the product of the molar volume V_i^* and the isobaric expansivity $\alpha^*_{p,i}$), $C^*_{p,i}$ (the isobaric molar heat capacity), and $K^*_{S,i}$, are properties of the pure liquid component i. The densities ρ of the mixture at the appropriate mole fraction used in the ultrasonic speed measurements were obtained from molar volumes of pure components and excess molar volumes from the cubic-spline interpolation reported in Refs. [4,5].

The deviations of the speeds of sound from their values in an ideal mixture were calculated from [27,28] :

$$u^D = u - u^{id}, \quad (6)$$

where

$$u^{id} = V^{id}_m / (K^{id}_{S,m} \cdot \Sigma x_i M_i)^{1/2}, \quad (7)$$

Also, the mixing function δu is defined :

$$\delta u = u - \Sigma x_i u_i^*, \quad (8)$$

For each mixture, the values of K^E_{Sm}, u^D, and δu were fitted to an equation of the type :

$$F(x) = (x_1 x_2) \sum_{i=0}^{k} a_i (x_1 - x_2)^i . \quad (9)$$

The values of the parameters a_i and the standard deviation σ are listed in Table 3(b). The values of u, K^E_{Sm}, u^D and δu together with their smoothed curves are shown in Figures 1 to 3.

The authors have attempted to explain the physico-chemical behaviour of the mixtures, such as molecular association and dissociation, as well as the strength and nature of interactions between the components by deriving various thermodynamic parameters, from the ultrasonic speed and density data. Parameters, such as, intermolecular free length [29] L_f, van der Waal's constant b, molecular

Table 3(a). Coefficient a_i and standard deviation σ of eq. (1) for u (ms^{-1}) of dipropylene glycol monobutyl ether + n-alcohols at 298.15 K.

$F(x)$	a_0	a_1	a_2	a_3		
			x_1 $C_4H_9[O(CH_2)_3]_2OH + x_2$ CH_3OH			
u (ms^{-1})	1107.4170	802.6578	−1649.8340	1624.4570	−607.1862	1.47
			x_1 $C_4H_9[O(CH_2)_3]_2OH + x_2$ C_3H_7OH			
u (ms^{-1})	1208.1440	259.7641	−450.0188	410.8951	−149.9756	0.47
			x_1 $C_4H_9[O(CH_2)_3]_2OH + x_2$ $C_5H_{11}OH$			
u (ms^{-1})	1274.9440	29.9394	−37.9032	12.2248		0.13
			x_1 $C_4H_9[O(CH_2)_3]_2OH + x_2$ $C_7H_{15}OH$			
u (ms^{-1})	1328.1890	−77.9196	74.1319	−79.9042	34.8537	0.11

Table 3(b). Coefficients a_i from eq. (9) and standard deviation (σ) for binary mixtures at 298.15 K.

$F(x)$	a_0	a_1	a_2	a_3	a_4	σ
			x_1 $C_4H_9[O(CH_2)_3]_2OH$ + x_2 CH_3OH			
δu (ms^{-1})	277.66	−184.71	117.08	−93.82	50.20	0.73
u^D (ms^{-1})	93.08	−88.48	67.56	−65.49	37.84	0.74
$K_{S,m}^E$ (mm^3 mol^{-1} MPa^{-1})	−17.15	6.67	−4.94	4.20		0.07
L_f^E (Å)	−0.2131	0.1479	−0.0975	0.1201	−0.0922	0.0004
Z^E (kg m^{-2}s^{-1})	446.6235	−285.9389	173.8823	−155.5478	96.9069	0.60
			x_1 $C_4H_9[O(CH_2)_3]_2OH$ + x_2 C_3H_7OH			
δu (ms^{-1})	92.9330	−50.6444	23.3292			0.72
u^D (ms^{-1})	55.3399	−44.9293	25.8430			0.71
$K_{S,m}^E$ (mm^3 mol^{-1} MPa^{-1})	−10.6413	4.7558	−4.8250	−0.7124	4.1380	0.08
L_f^E (Å)	−0.0840	0.0507	−0.0276			0.0004
Z^E (kg m^{-2} s^{-1})	211.4909	−106.2646	66.2663	−11.8750	−22.8247	0.57
			x_1 $C_4H_9[O(CH_2)_3]_2OH$ + x_2 $C_5H_{11}OH$			
δu (ms^{-1})	19.19	−5.18	−0.22	−2.77		0.13
u^D (ms^{-1})	24.51	−9.33	2.21	−3.86		0.13
$K_{S,m}^E$ (mm^3 mol^{-1} MPa^{-1})	−5.94	0.83	−0.99	1.05	0.77	0.02
L_f^E (Å)	−0.0326	0.0114	−0.0040	0.0032		0.0001
Z^E (kg m^{-2} s^{-1})	103.8953	−32.0893	11.5988	−7.8811		0.11
			x_1 $C_4H_9[O(CH_2)_3]_2OH$ + x_2 $C_7H_{15}OH$			
δu (ms^{-1})	−13.89	5.58	−14.38	−5.79	15.49	0.13
u^D (ms^{-1})	10.27	−0.27	−13.05	−6.31	16.06	0.13
$K_{S,m}^E$ (mm^3 mol^{-1} MPa^{-1})	−2.91	0.10	1.66	1.38	−2.47	0.02
L_f^E (Å)	−0.0080	0.0014	0.0050	0.0026	−0.0079	0.0001
Z^E (kg m^{-2} s^{-1})	41.9672	−7.6280	−6.6079	−7.3568	12.7988	0.11

radius [29] r, geometrical volume B, molecular surface area Y, available volume [30] V_a, molar speed of sound [31] R, collision factor [32] S, specific acoustic impedance [33] Z, relative association [34] R_A, and molecular association [35] M_A have been calculated using the following relations :

$$L_f = K/(u\cdot\rho^{1/2}), \tag{10}$$

$$b = (M/\rho) - (RT/\rho u^2)\{[1 + (Mu^2/3RT)]^{1/2} - 1\}, \tag{11}$$

$$r = (3b/16\pi N)^{1/3}, \tag{12}$$

$$B = (4/3)\pi r^3 N, \tag{13}$$

$$Y = (36\pi NB^2)^{1/3}, \tag{14}$$

$$V_a = V(1 - u/u_\infty), \tag{15}$$

$$V_\theta = V - V_a, \tag{16}$$

$$R = M\cdot u^{1/3}/\rho, \tag{17}$$

$$S = uV_m/u_\infty B, \tag{18}$$

$$Z = u\rho, \tag{19}$$

$$R_A = (\rho_{mix}/\rho)\ (u/u_{mix})^{1/3}, \tag{20}$$

$$M_A = [(u_{mix}/\Sigma x_i u_i^*)^2 - 1], \tag{21}$$

where L_f is the free length of ideal mixing, K is a temperature dependence constant (= (93.875 + 0.375 T) $\times 10^{-8}$) [29], V_0 is a volume at absolute zero, u_∞ is taken as 1600 ms^{-1}. These parameters are listed in Table 4 for the pure components.

The variations of V_a, R_A, Z, L_f, R, and M_A for mixtures with mole fraction x_1 of ether are given in Table 5. It is observed from Tables 2 and 5 that $K_{S,m}$, R, and Z increase with mole fraction of x_1, while R_A increases except with methanol and L_f decreases for all the mixtures. It may be compared with dipropylene glycol monomethyl ether + n-alkanol systems [2] : R_A increases with mole fraction for all mixtures. Relatively higher values of R_A for dipropylene glycol monomethyl ether [2] or dipropylene glycol monobutyl ether-methanol systems, signify that unlike interactions are relatively stronger than like interactions, the former tends to increase while the latter causes a

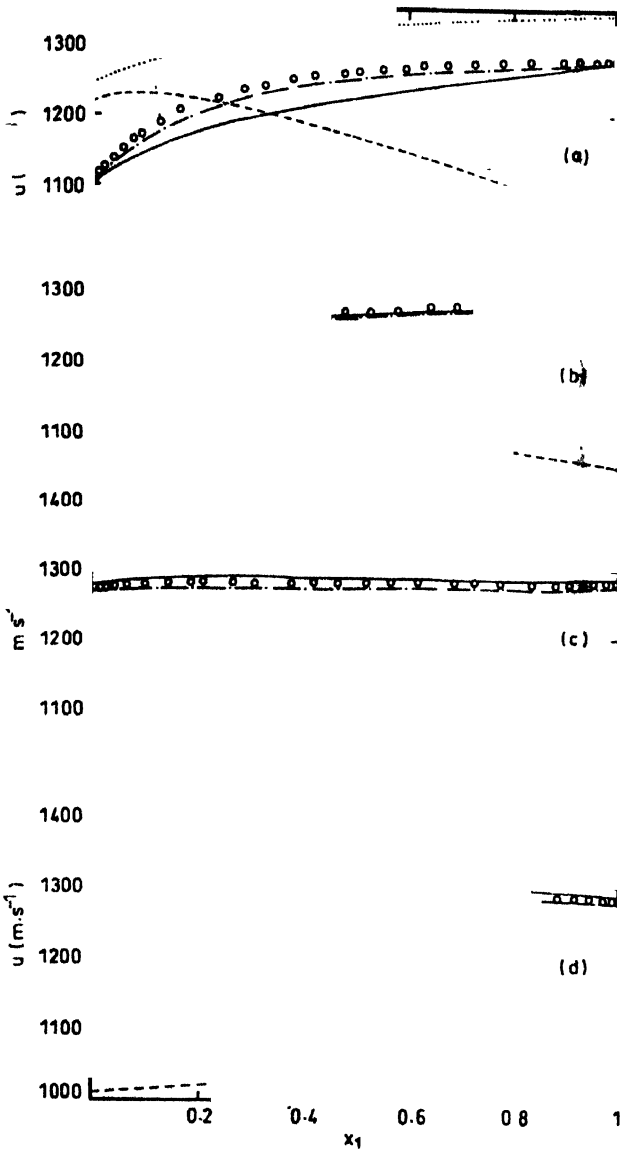

Figure 1. Experimental and calculated ultrasonic speeds u (ooooo); u_{CFT} (——); u_J (.....); u_N (–·–·–); u_{FLT} (– – –) for $x_1C_4H_9[O(CH_2)_3]_2OH$ + x_2CH_3OH, (a); + $x_2C_3H_7OH$, (b); + $x_2C_5H_{11}OH$, (c); + $x_2C_7H_{15}OH$, (d) at 298.15 K.

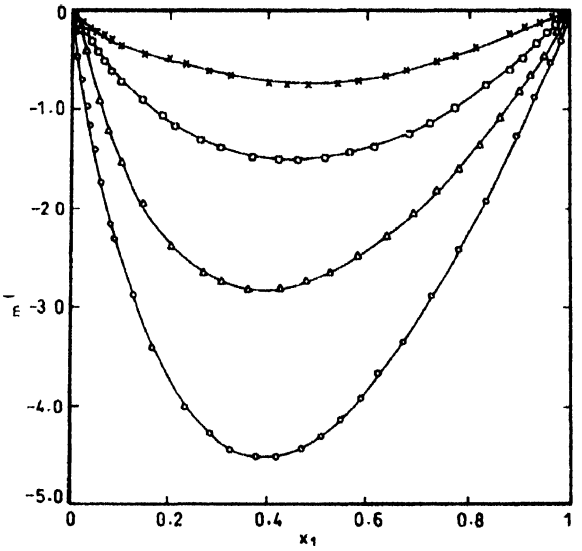

Figure 2. Variation of $K^E_{S,m}$ at 298.15 K for $x_1C_4H_9[O(CH_2)_3]_2OH$ + x_2CH_3OH (o); + $x_2C_3H_7OH$ (Δ); + $x_2C_5H_{11}OH$ (□); + $x_2C_7H_{15}OH$ (×). Continuous curves calculated from eq. (9).

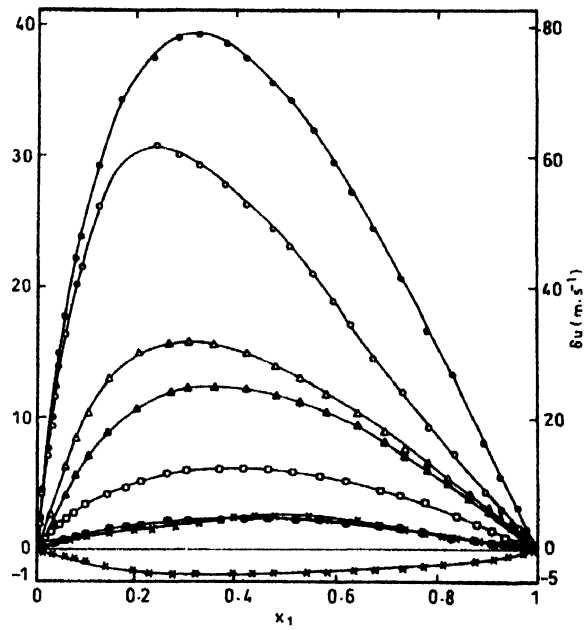

Figure 3. Variation of u^D (o, Δ, □, ×) and δu (• ▲, ■, *), for $x_1C_4H_9[O(CH_2)_3]_2OH + x_2CH_3OH$ (o, •); + $x_2C_3H_7OH$ (Δ, ▲); + $x_2C_5H_{11}OH$ (□, ■); + $x_2C_7H_{15}OH$ (×, *) at 298.15 K. Continuous curves calculated from eq. (9).

decrease in R_A. The increase in u and the corresponding decrease in $K^E_{S,m}$ and L_f with x_1 indicates significant interactions between dipropylene glycol monomethyl ether [2] or dipropylene glycol monobutyl ether and lower

Table 4. Values of the derived parameters of the pure components at 298.15 K.

Components	$b \times 10^6$ (m³)	r (nm)	$B \times 10^6$ (m³ mol⁻¹)	S	$R \times 10^6$ (m³ mol⁻¹) (ms⁻¹)$^{1/3}$	$V_a \times 10^6$ (m³ mol⁻¹)	L_f (Å)	$V_0 \times 10^6$ (m³ mol⁻¹)	Y (Å)	$Z \times 10^{-3}$ (kg m⁻¹ s⁻¹)
$C_4H_9[O(CH_2)_3]_2OH$	203.86	0.272	50.74	3.30	2273	41.97	0.5342	167.49	55.96	1162.44
CH_3OH	36.87	0.154	9.22	3.05	421	12.59	0.6644	28.15	17.95	869.50
C_3H_7OH	69.69	0.190	17.30	3.29	801	18.33	0.6022	56.82	27.31	967.29
$C_5H_{11}OH$	102.09	0.216	25.41	3.41	1178	22.07	0.5673	86.60	35.29	1034.18
$C_7H_{15}OH$	134.39	0.237	33.57	3.51	1559	24.14	0.5421	117.71	42.49	1087.66

Table 5. Available volume V_a (m^3 mol^{-1}), relative association R_A, specific acoustic impedance Z (kg m^{-2} s^{-1}), intermolecular free length L_f (Å), molar speed of sound R {m^3 mol^{-1} $(ms^{-1})^{1/3}$} and molecular association M_A for dipropylene glycol monobutyl ether + *n*-alcohol mixtures at 298.15 K.

x_1	$V_a \times 10^6$	R_A	$Z \times 10^{-3}$	L_f	$R \times 10^6$	M_A
			X_1 $C_4H_9[O(CH_2)_3]_2OH$ + x_2 CH_3OH			
0.0022	12.65	1.0006	872.66	0.6626	425	0.0027
0.0072	12.80	1.0007	879.65	0.6587	434	0.0088
0.0139	12.98	1.0007	888.98	0.6536	447	0.0172
0.0233	12.24	1.0008	901.21	0.6470	464	0.0279
0.0317	13.47	1.0009	911.60	0.6414	479	0.0369
0.0396	13.69	1.0009	920.87	0.6366	494	0.0448
0.0492	13.94	1.0008	931.73	0.6310	511	0.0541
0.0604	14.22	1.0007	943.85	0.6248	532	0.0646
0.0810	14.76	1.0005	963.78	0.6150	570	0.0808
0.0910	15.04	1.0005	972.30	0.6110	588	0.0869
0.1274	16.01	1.0003	1000.41	0.5980	655	0.1066
0.1690	16.93	0.9988	1030.37	0.5842	733	0.1302
0.2375	18.94	0.9996	1060.14	0.5722	858	0.1363
0.2887	20.31	0.9992	1079.70	0.5643	953	0.1407
0.3289	21.41	0.9991	1092.10	0.5594	1028	0.1404
0.3799	22.83	0.9990	1105.21	0.5544	1122	0.1371
0.4213	24.01	0.9990	1114.20	0.5510	1199	0.1324
0.4739	24.51	0.9980	1123.67	0.5475	1296	0.1247
0.5095	26.55	0.9990	1129.20	0.5455	1362	0.1186
0.5514	27.79	0.9991	1134.75	0.5435	1440	0.1103
0.5932	29.06	0.9993	1139.40	0.5419	1517	0.1012
0.6290	30.16	0.9992	1142.82	0.5407	1583	0.0928
0.6736	31.54	0.9993	1146.52	0.5395	1666	0.0821
0.7249	33.17	0.9995	1150.02	0.5383	1761	0.0692
0.7817	34.94	0.9996	1153.67	0.5371	1867	0.0554
0.8302	36.47	0.9996	1156.26	0.5362	1957	0.0433
0.8963	38.59	0.9998	1159.07	0.5353	2080	0.0265
0.9288	39.63	0.9998	1160.32	0.5348	2141	0.0183
0.9590	40.63	0.9998	1161.21	0.5346	2197	0.0104
0.9786	41.25	0.9999	1161.95	0.5343	2234	0.0057
0.9924	41.74	1.0000	1162.12	0.5343	2259	0.0018
			x_1 $C_4H_9[O(CH_2)_3]_2OH$ + x_2 C_3H_7OH			
0.0060	18.51	0.9770	969.93	0.6013	809	0.0000
0.0118	18.65	0.9775	972.93	0.6001	818	0.0010
0.0215	18.89	0.9783	977.64	0.5983	832	0.0022
0.0347	19.15	0.9790	985.00	0.5953	851	0.0061
0.0568	19.52	0.9797	997.71	0.5899	884	0.0143
0.0783	19.96	0.9807	1007.97	0.5859	916	0.0189
0.1043	20.51	0.9819	1019.41	0.5814	954	0.0237
0.1464	21.41	0.9837	1035.94	0.5753	1016	0.0297
0.2038	22.65	0.9857	1055.42	0.5682	1100	0.0358
0.2710	24.16	0.9879	1074.02	0.5617	1199	0.0392
0.3082	25.00	0.9889	1083.02	0.5586	1254	0.0403
0.3582	26.15	0.9901	1093.84	0.5550	1327	0.0409
0.4276	27.78	0.9917	1106.57	0.5508	1430	0.0398
0.4821	29.06	0.9928	1115.29	0.5480	1510	0.0382
0.5284	30.17	0.9936	1121.87	0.5460	1578	0.0363
0.5778	31.36	0.9945	1128.15	0.5441	1651	0.0337
0.6370	32.80	0.9954	1134.91	0.5420	1738	0.0302
0.6904	34.11	0.9962	1140.42	0.5404	1817	0.0266
0.7351	35.23	0.9969	1144.35	0.5392	1883	0.0230
0.7784	36.30	0.9974	1148.16	0.5381	1947	0.0199
0.8214	37.38	0.9979	1151.48	0.5372	2010	0.0164
0.8617	38.40	0.9984	1154.29	0.5364	2069	0.0128
0.9007	39.39	0.9989	1156.90	0.5357	2127	0.0095
0.9174	39.83	0.9991	1157.83	0.5354	2152	0.0078
0.9446	40.52	0.9994	1159.53	0.5349	2192	0.0054
0.9719	41.26	0.9997	1160.81	0.5346	2232	0.0024
0.9968	41.90	1.0000	1162.20	0.5343	2269	0.0002
			x_1 $C_4H_9[O(CH_2)_3]_2OH$ + x_2 $C_5H_{11}OH$			
0.0039	22.15	0.9642	1035.27	0.5670	1183	0.0001
0.0110	22.28	0.9648	1037.16	0.5664	1190	0.0002
0.0219	22.49	0.9656	1039.97	0.5657	1202	0.0003
0.0311	22.65	0.9662	1042.55	0.5649	1212	0.0009
0.0430	22.86	0.9670	1045.72	0.5639	1225	0.0014
0.0552	23.08	0.9677	1048.90	0.5630	1238	0.0020
0.0661	23.27	0.9684	1051.63	0.5622	1250	0.0024
0.0773	23.46	0.9691	1054.53	0.5613	1262	0.0031
0.0977	23.83	0.9703	1059.43	0.5599	1284	0.0039
0.1470	24.76	0.9731	1069.96	0.5570	1338	0.0047
0.1852	25.48	0.9751	1077.56	0.5549	1380	0.0053
0.2145	26.03	0.9765	1083.12	0.5533	1412	0.0059
0.2668	27.01	0.9789	1092.35	0.5508	1469	0.0068
0.3067	27.78	0.9806	1098.74	0.5491	1513	0.0072
0.3709	29.02	0.9831	1108.16	0.5467	1513	0.0075
0.4208	30.00	0.9850	1114.74	0.5450	1638	0.0075
0.4680	30.92	0.9865	1120.65	0.5435	1689	0.0077
0.5205	31.97	0.9883	1126.50	0.5421	1747	0.0073
0.5672	32.91	0.9897	1131.37	0.5409	1798	0.0070
0.6216	34.00	0.9912	1136.66	0.5397	1858	0.0066
0.6874	35.34	0.9930	1142.39	0.5384	1930	0.0059
0.7248	36.12	0.9939	1145.36	0.5377	1971	0.0053
0.7751	37.18	0.9952	1149.00	0.5369	2026	0.0043
0.8312	38.38	0.9965	1152.72	0.5362	2088	0.0032
0.8765	39.33	0.9975	1155.60	0.5356	2137	0.0024
0.9048	39.93	0.9981	1157.31	0.5352	2169	0.0019
0.9363	40.61	0.9988	1159.05	0.5349	2203	0.0012
0.9497	40.92	0.9991	1159.62	0.5348	2218	0.0007

Table 5. *Cont'd.*

0.9768	41.49	0.9996	1161.17	0.5345	2248	0.0003
0.9967	41.93	1.0000	1162.30	0.5342	2271	0.0000
		x_1 $C_4H_9[O(CH_2)_3]_2OH$ + x_2 $C_7H_{15}OH$				
0.0060	24.23	0.9545	1088.62	0.5419	1563	0.0001
0.0142	24.35	0.9551	1089.81	0.5417	1569	0.0001
0.0234	24.52	0.9557	1090.92	0.5415	1576	−0.0003
0.0363	24.75	0.9566	1092.51	0.5413	1585	−0.0007
0.0494	24.98	0.9575	1094.08	0.5411	1594	−0.0011
0.0638	25.23	0.9585	1095.76	0.5409	1604	−0.0015
0.0807	25.54	0.9596	1097.65	0.5407	1616	−0.0021
0.1003	25.88	0.9609	1099.84	0.5404	1630	−0.0026
0.1471	26.72	0.9638	1104.83	0.5398	1663	−0.0038
0.1991	27.62	0.9668	1110.17	0.5391	1700	−0.0045
0.2308	28.20	0.9687	1113.07	0.5388	1722	−0.0052
0.2788	29.02	0.9712	1117.68	0.5382	1756	−0.0053
0.3287	29.90	0.9737	1121.97	0.5377	1792	−0.0058
0.3973	31.09	0.9770	1127.79	0.5370	1841	−0.0056
0.4394	31.81	0.9789	1131.16	0.5366	1871	−0.0054
0.4784	32.51	0.9807	1133.98	0.5363	1899	−0.0054
0.5432	33.67	0.9835	1138.48	0.5359	1946	−0.0052
0.5831	34.39	0.9852	1141.01	0.5357	1974	−0.0052
0.6404	35.41	0.9875	1144.67	0.5353	2015	−0.0046
0.6817	36.20	0.9892	1146.73	0.5353	2045	−0.0049
0.7304	37.06	0.9910	1149.59	0.5350	2080	−0.0042
0.7746	37.87	0.9926	1151.95	0.5348	2111	−0.0037
0.8145	38.62	0.9941	1153.81	0.5348	2140	−0.0035
0.8813	39.81	0.9963	1157.19	0.5345	2188	−0.0022
0.9125	40.41	0.9973	1158.42	0.5345	2210	−0.0021
0.9425	40.94	0.9983	1159.85	0.5344	2232	−0.0014
0.9634	41.32	0.9989	1160.80	0.5343	2247	−0.0009
0.9827	41.66	0.9995	1161.70	0.5342	2261	−0.0004
0.9970	41.92	0.9999	1162.31	0.5342	2271	−0.0001

alcohol molecules, however there is less decrease in $K^E_{S,m}$ in dipropylene glycol monobutyl ether than in dipropylene glycol monomethyl ether [2]. The addition of dipropylene glycol monobutyl ether tends to cause breaking of associates in alcohol molecules or both, with a consequent increase in u or decrease in L_f with x_1. However, because of simultaneous interactions, mainly due to possible association through hydrogen-bonding interaction of the O–H---O between unlike molecules, there is a compensating effect resulting in overall increase in V_a and u or decrease in $K^E_{S,m}$, and L_f with x_1.

Both the values of the acoustic impedance Z and the molar speed of sound R for dipropylene glycol monomethyl ether [2] or dipropylene glycol monobutyl ether, increase with increasing x_1 for all mixtures, whereas the values of Z and R are slightly lower for dipropylene glycol monobutyl ether at higher x_1 The large positive deviation in M_A are observed with methanol and these deviations decrease in the order : methanol >1-propanol >1-pentanol >1-heptanol. Thus, it is concluded that the non-ideality of the systems varies in the order : 1-heptanol < 1-pentanol < 1-propanol < methanol.

The excess functions of intermolecular free length and acoustic impedance Z were calculated using the relation

$$L_f^E = L_f - [x_1 L_{f,1} + x_2 L_{f,2}], \quad (22)$$

$$Z^E = Z - [x_1 Z_1 + x_2 Z_2]. \quad (23)$$

The results of L_f^E and Z^E were fitted to a polynomial similar to that given by eq. (9). Parameters a_i along with standard deviations σ are listed in Table 3(b) and are graphically represented in Figure 4.

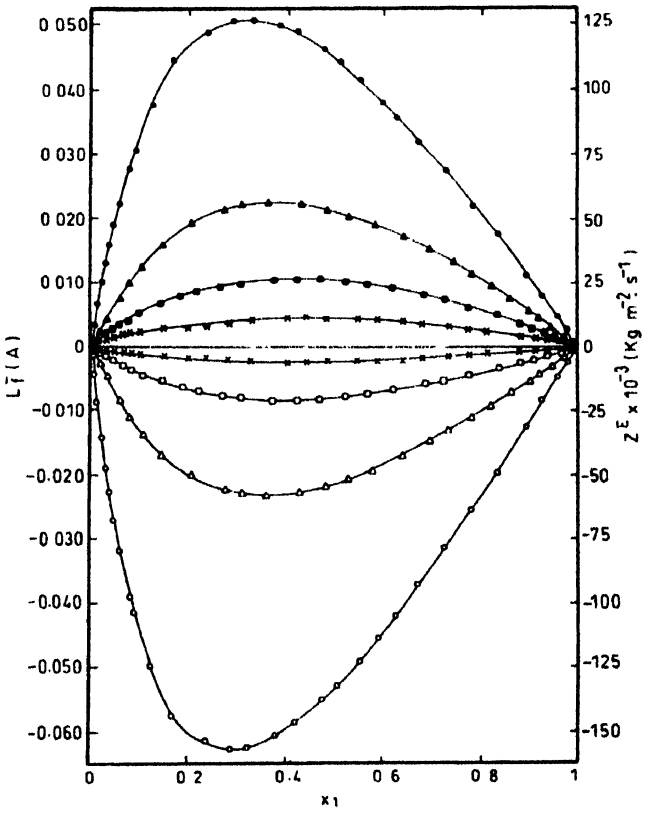

Figure 4. Variation of excess intermolecular free length L_f^E (o, Δ, □, ×) and excess acoustic impedance Z^E (•, ▲, ■, *) for $x_1C_4H_9[O(CH_2)_3]_2OH$ + x_2CH_3OH (o, •); + $x_2C_3H_7OH$ (Δ, ▲); + $x_2C_5H_{11}OH$ (□, ■); + $x_2C_7H_{15}OH$ (×, *) at 298.15 K. Continuous curves calculated from eq. (9).

Figure 4 shows that L_f^E are negative while Z^E are positive for all mixtures over the entire composition range. Negative or positive deviations in these functions from rectilinear dependence on composition of the mixtures, indicate the extent of association or dissociation

between unlike molecules. The observed very large negative values of $K_{S,m}^E$ and L_f^E can be accounted only by considering the predominance of the formation of O–H---O bond over the rupture of hydrogen bond present in pure ether and alcohol. It is interesting to note that $K_{S,m}^E$ and L_f^E become more negative with methanol than the higher alcohols. The observed behaviour of $K_{S,m}^E$ and L_f^E (Figures 2 and 4) for dipropylene glycol monobutyl ether + methanol binary mixtures, supports the conclusion drawn from the V_m^E values [4,5]. Further, increasingly positive values of Z^E with x_1 (Figure 4) are indicative of the increasing strength of interaction between the component molecules of the mixtures, as suggested by Tiwari *et al* [36].

For all the mixtures studied, $K_{S,m}^E$ is negative over the whole mole fraction range for dipropylene glycol monobutyl ether or dipropylene glycol monomethyl ether [2] and shows a minimum in the sequence : methanol > 1-propanol > 1-pentanol > 1-heptanol. The $K_{S,m}^E$ is more negative for dipropylene glycol monomethyl ether [2] than dipropylene glycol monobutyl ether and the minimum is shifted to lower values of x_1 in the same sequences in both the cases. The overall behaviour of $K_{S,m}^E$ is similar for u^D but of opposite sign. Also, the behaviour of excess molar volume [5] seems to be consistent with a minimum value of $K_{S,n}^E$ and a maximum value for u^D of dipropylene glycol monobutyl ether with methanol. This is normal because u is generally higher for a rigid structure. Negative values of $K_{S,m}^E$ mean that the mixture is less compressible than the corresponding ideal mixture, suggesting that there may be strong intermolecular hydrogen bonding with lower alcohols. As the ether is added to alcohols, thereby causing a break down of self-associated ether or both, and hence contribute to a dense packing of the molecules through hydrogen bonding, increasing u and decreasing $K_{S,m}^E$. However, V_m^E [4,5] is less negative for higher alcohols, although $K_{S,m}^E$ is negative and u^D is likewise positive from methanol to 1-heptanol, indicating that when the mixture is created, the 'excess free volume' increases and is higher in mixtures containing dipropylene glycol monobutyl ether and methanol. Again, the effect is that with increasing the chain length of the *n*-alkanol, interstitial accommodation becomes less important that the molecules of two components cannot accommodate easily. This additional rigidity is a good reason for the positive values of u^D.

The present results for $K_{S,m}^E$ and u^D for dipropylene glycol monobutyl ether, support the conclusion drawn from the values of V_m^E. Finally, we find in Figure 4, a similar variation of u^D and δu with the chain length of *n*-alkanol, while $K_{S,m}^E$ shows opposite variation. Thus, $K_{S,m}^E$ and δu can not be correlated well.

For comparison, we have calculated the theoretical values of the ultrasonic speeds from the following empirical equations :

Collision factor theory [30] :

$$u_{CFT} = u_\infty\{x_1S_1 + x_2S_2\}[\{x_1B_1 + x_2B_2\}/V]. \quad (24)$$

Free length theory [29] :

$$u_{FLT} = K/(L_f\rho^{1/2}). \quad (25)$$

Junjie equation [37] :

$$u_J = \{(x_1M_1/\rho_1) + (x_2M_2/\rho_2)\}/[\{x_1M_1 + x_2M_2\}^{1/2} \times\{(x_1M_1/\rho_1u_1^2) + (x_2M_2/\rho_2u_2^2)\}^{1/2}]. \quad (26)$$

Nomoto equation [38] :

$$u_N = [\{x_1R_1 + x_2R_2\}/\{x_1V_1 + x_2V_2\}]^3. \quad (27)$$

The computed U_{CFT}, U_{FLT}, U_J, and U_N values are shown in Figure 1 for comparison with experimental values, for all the mixtures. As can be seen, the collision factor theory and Nomoto expression predict the experimental data extremely well, for all the mixtures. However, there are significant deviations in Junjie and free length theory for all the mixtures.

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